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<b>(21) International Application Number:</b> PCT/AU00/00460 <b>(22) International Filing Date:</b> 15 May 2000 (15.05.00)  <b>(30) Priority Data:</b> 60/134,454      17 May 1999 (17.05.99)      US  <b>(71) Applicant (for all designated States except US):</b> KNOX, John, Andrew [AU/AU]; 57 Tyrell Street, Nedlands, Western Australia 6009 (AU).  <b>(71)(72) Applicant and Inventor:</b> PRETORIUS, Hendrik, Johannes, Gideon [ZA/ZA]; 4 Bach Avenue, 2520 Potchefstroom (ZA).  <b>(74) Agent:</b> MCSTEA, John, Anthony; MBT (Schweiz) AG, Patents And Trade Marks, Vulkanstrasse 110, CH-8048 Zürich (CH).		<b>(81) Designated States:</b> AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> POLYMERIC STRUCTURAL SUPPORT MEMBRANE  <b>(57) Abstract</b> <p>In excavations, such as mines, supports are needed to prevent rock falls. Structural beams provide the main support in the excavation to prevent major rock falls. However, between the main beams, minor rock falls can still occur. To provide structural support between the main beams, a polymeric structural support membrane can be applied. The membrane includes a polymer that is the reaction product of monomer, an initiator, and optionally a crosslinking agent; and a self-extinguishing agent. The membrane can be applied by spraying, brushing, or rolling.</p>		

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## POLYMERIC STRUCTURAL SUPPORT MEMBRANE

### FIELD OF THE INVENTION

5       The present invention is directed to structural support coverings for excavations, such as mines. More particularly, the present invention is directed to a polymeric membrane that is applied to the surfaces of an excavation to provide structural support.

### 10       BACKGROUND OF THE INVENTION

When ground is excavated, structural supports are placed in the excavation to prevent the ground from collapsing into the excavated area. Mainly, the ground is supported by support rods that are placed along the excavation. These supports are typically steel reinforcing rods that are held in place by mechanical anchors and/or  
15       grouts. These supports provide the main protection against unplanned rock falls.

The excavation, however, exposes natural rock features, such as faults and joints, and can damage the ground by digging or blasting. Minor rock falls can occur  
20       between the main supports. Even though they may be isolated or relatively small, they still pose a hazard to people working in the excavation.

To prevent these minor rock falls between the supports, wire screens or mesh have been installed between the main supports. There are many disadvantages to  
25       using a wire screen. The screen requires labor-intensive installation. The screen offers no protection against weathering of the rock face. Because of the unevenness of the rock face, the screen is not fully flush with the rock face. The screen only becomes effective after considerable rock movement puts tension on the screen. The screen is prone to corrosion and deterioration. The screen is prone to blasting damage  
30       if it is installed close to the advancing face. Because it cannot be installed remotely, it is hazardous to install because of falling rock. It can be difficult to cover with

shotcrete, relatively high rebound and lower substrate adhesion being commonly-encountered problems.

One possible alternative to a wire mesh would be to spray concrete (shotcrete) on to the rock face. However, this would be expensive to apply to all surfaces in an excavation. In addition, shotcreting may not be possible in all locations.

Sealants have been used in mines to prevent air leaks. Sealants, however, are not capable of providing structural support to a surface in an excavation. Generally, sealants are aqueous dispersions of polymer. Because of the water content, they cannot be applied to a surface at a thickness sufficient to provide support. Moreover, the aqueous dispersion prohibits quick setting of the polymer on the surface, which in turn does not provide sufficient tensile strength.

What is needed in the art is a structural membrane that can be installed with minimal labor, can be installed remotely from the exposed rock face, offers weathering protection to the rock face, does not corrode, becomes effective with minimal rock deformation, can be applied near the advancing face, is less prone to blast damage, and can be covered with shotcrete if deemed necessary.

It is an object of the invention to provide a polymeric structural support membrane for providing support to exposed surfaces in an excavation.

It is another object of the invention to provide a polymeric structural support membrane that has a tensile strength, thickness, and molecular weight that are sufficient to provide support to exposed surfaces in an excavation.

## SUMMARY OF THE INVENTION

The present invention provides a polymeric excavation structural support membrane comprising a polymer that is the initiator-induced reaction product of monomer; a self-extinguishing agent; and optionally at least one of a crosslinking

agent, a rheology modifier, reaction rate modifier, plasticizer, emulsifier, defoamer, filler, wet surface adhesion modifier, and coloring agent; wherein the monomer is selected from the group consisting of alkyl ester acrylates, alkyl ester methacrylates, and mixtures thereof; wherein the membrane has a tensile strength, a thickness, and a molecular weight sufficient to provide support to exposed surfaces in an excavation.

The present invention also provides a method of reinforcing exposed surfaces in an excavation with a polymeric structural support membrane comprising: providing a mixture of a polymer that is the initiator-induced reaction product of monomer; a self-extinguishing agent; and optionally at least one of a crosslinking agent, a rheology modifier, reaction rate modifier, plasticizer, emulsifier, defoamer, filler, wet surface adhesion modifier, and coloring agent; wherein the monomer is selected from the group consisting of alkyl ester acrylates, alkyl ester methacrylates, and mixtures thereof; wherein the membrane has a tensile strength, a thickness, and a molecular weight sufficient to provide support to exposed surfaces in an excavation; and applying said mixture to an exposed surface in an excavation.

The monomer is ethylenically-unsaturated monomer and is preferably selected from the group consisting of monofunctional alkyl ester acrylates, monofunctional alkyl ester methacrylates, and mixtures thereof.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a polymeric structural support membrane for excavations. The membrane includes a polymer and a self-extinguishing agent.

The polymer is a reaction product of monomer selected from the group consisting of monofunctional monomers, di-functional monomers, tri-functional monomers, tetra-functional monomers, and mixtures thereof. By "functional", it is meant that the monomer has at least one ethylenic double bond which is capable of participating in an addition polymerization reaction to form a polymer. The term also

includes the case where the monomer may additionally have one or more functional groups which allow the possibility of crosslinking the polymer chains. Such groups can be ethylenic double bonds, or they may be other reactive groups (such as hydroxyl, carboxyl and amino groups) which can give rise to crosslinking by means of a crosslinking agent. It is preferred that further functionality above the level of monofunctional be supplied by additional ethylenic double bonds. It is possible to utilise a mixture of various monomers of different functionalities.

The polymer is present in the membrane in an amount that provides the membrane with a tensile strength and a thickness, and it has a molecular weight, sufficient to provide support to exposed surfaces in an excavation. The polymer is generally present in an amount from about 30% to about 70% based on the weight of the membrane. In one embodiment, the polymer is present in the membrane from about 51% to about 70% based on the weight of the membrane.

The monofunctional monomers used according to the present invention are monofunctional esters, particularly monofunctional alkyl ester acrylates, monofunctional alkyl ester methacrylates, and mixtures thereof. The methacrylates are preferred because they produce less odour.

Examples of useful monofunctional alkyl ester acrylates and monofunctional alkyl ester methacrylates include, but are not limited to alkyl acrylates and methacrylates and mixtures thereof. Lauryl and stearyl methacrylates are particularly useful materials, as they provide a plasticising effect.

The di-functional monomers can be any di-functional alkyl ester. Di-functional esters that can be used are di-functional alkyl acrylates, di-functional alkyl methacrylates, and mixtures thereof. An example of a di-functional alkyl ester is ethylene glycol dimethacrylate. Examples of di-functional monomers having non-ethylenic groups as additional functionality include hydroxy propyl methacrylate and hydroxy ethyl methacrylate.

The tri-functional monomers can be any di-functional ester. Tri-functional esters that can be used are tri-functional acrylates, tri-functional methacrylates, and mixtures thereof. An example of a tri-functional ester is ethoxylated trimethylol propane triacrylate.

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The tetra-functional monomers can be any tetra-functional alkyl ester. Tetra-functional esters that can be used are tetra-functional acrylates, tetra-functional methacrylates, and mixtures thereof. An example of a tetra-functional ester is pentaacrylate ester.

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Preferably, the polymer is the reaction product of a monomer selected from the group consisting of monofunctional alkyl ester acrylates, monofunctional alkyl ester methacrylates, and mixtures thereof, and a crosslinking agent.

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When a monofunctional monomer is selected, a crosslinking agent is reacted with the monomer to provide crosslinking between the polymer chains to provide structural support. Suitable examples of the crosslinking agent include, but are not limited to, methylene bis acrylamide, polymethylmethacrylate, butadiene styrene acrylate, styrene butyl acrylate copolymer, 1,6-hexanediol dimethacrylate, ethoxylated bisphenol A dimethacrylate, polyethylene glycol dimethacrylate, and mixtures thereof. The crosslinking agent can be present up to about 30% based on the weight of the monomer.

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Because the membrane is being applied in an excavation, particularly in a mine, there is the potential for fire. In each jurisdiction, there are requirements that the membrane be self-extinguishing. The test is performed by holding the membrane to a flame for a fixed period of time. The membrane must then self-extinguish within a set maximum time.

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Provided in the membrane is a self-extinguishing agent. The self-extinguishing agent can be any material that provides self-extinguishing properties to the membrane.

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Suitable examples of self-extinguishing agents include, but are not limited to, phosphates, such as triphenyl phosphate or tri-(2-chloroethyl) phosphate, exfoliated graphite (which can be acid-treated natural graphite flakes), and mixtures thereof. The self-extinguishing agent is present in the membrane from about 5 to about 40% based on the weight of the membrane.

The gel and set time of the membrane can be controlled by adding at least one initiator. The initiator can be an oxidizing agent. Suitable oxidizing agents include, but are not limited to, peroxides, such as benzoyl peroxide, dibenzoyl peroxide, persulfates, such as ammonium persulfate, and mixtures thereof. The initiator is added in an amount from about 1% to about 10% based on the weight of the monomer.

In combination with the initiator, a reaction rate modifier, such as an accelerator, can be added. The reaction rate modifier can be a reducing agent. Suitable reducing agents include, but are not limited to, aniline-containing compounds, amines, glycols, octoates, and mixtures thereof. Suitable examples of the reaction rate modifier include, but are not limited to, triethanolamine, N,N-dimethyl-p-toluidine, and tripropyl amines. The reaction rate modifier can be present in an amount up to about 10% based on the weight of the monomer.

The materials to form the membrane can either be provided as a single composition, or the materials can be provided as a two component formulation. The two component system may be desired when an initiator and a reaction rate modifier are being provided for in the membrane. In this instance, the initiator would be supplied in one component, and the reaction rate modifier could be supplied in the other component.

The membrane can also include a rheology modifier to increase the viscosity of the membrane materials immediately after application to excavation surfaces. This may be desired to prevent the membrane from slumping before it cures when it is



applied to a surface in an excavation. Suitable examples of the rheology modifier include fumed silica, hydroxyethyl cellulose, hydropropyl cellulose, fly ash (as defined in ASTM C618), mineral oils (such as light naphthenic), tetra alkyl ammonium hectorite clay, any other solids that are inert to the other materials in the membrane, and mixtures thereof. The rheology modifier can be present in an amount up to about 10% based on the weight of the membrane.

The membrane can also include an emulsifier. It may be desired to add an emulsifier to increase the adhesion of the membrane to a surface. The emulsifier can be any anionic surfactant or nonionic surfactant. Suitable examples of the emulsifier include, but are not limited to, ethoxylated nonyl phenols (preferably with 4-10 ethylene oxide units), lauryl sulfates and mixtures thereof. The emulsifier can be present in an amount up to about 5% based on the weight of the monomer.

The membrane can also contain a plasticizer to make the membrane more flexible. The plasticizer can be any material that plasticizes the polymer in the membrane. Suitable examples of the plasticizer include, but are not limited to, lauryl methacrylates and stearyl methacrylates. The plasticizer can be present in an amount up to about 40% based on the weight of the monomer.

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The membrane can also include a filler. Suitable examples of the filler include, but are not limited to glass, such as crushed glass, quartz, silica, barytes, limestone, sulfates, alumina, various clays, diatomaceous earth, wollastonite, mica, perlite, flint powder, kryolite, alumina trihydrate, talc, sand, pyrophyllite, granulated polyethylene, aluminum oxide, zinc oxide, titanium dioxide, and mixtures thereof. A preferred filler is titanium dioxide. The filler can be present in an amount up to about 40% based on the weight of the monomer.

The membrane can also include a wet surface adhesion modifier. The wet surface adhesion modifier provides for increased adhesion to wet surfaces. The wet surface adhesion modifier can be any material that increases the adhesion of the

membrane to a wet surface. Suitable examples of the wet surface adhesion modifier include, but are not limited to, metallic acrylate or methacrylate at up to about 3% of total monomer content, ammonium oleate, magnesium oleate, ammonium acrylate and metal borates. A preferred wet surface adhesion modifier is zinc borate. The wet  
5 surface adhesion modifier is preferably present in an amount up to about 3% based on the weight of the monomer.

The membrane can also include a colouring agent, such as a pigment or a dye, to provide a desired color to the membrane. An example of a colouring agent is  
10 titanium dioxide, but other colouring agents are also useful. The colouring agent can be present in an amount up to about 3% based on the weight of the monomer.

The membrane can also include a defoamer such as a modified silicone or a petroleum oil mixture. A preferred defoamer is FOAMASTER™ S available from Cognis Corporation, Cincinnati, Ohio. The defoamer can be present in an amount up  
15 to about 3% based on the weight of the monomer.

A preferred membrane is formed from a two-component reaction mixture. The first component includes the monomer and the crosslinking agent that react to become the polymer, and any other additive. The second component includes the  
20 initiator and any other additive. The two-component mixture is preferred so that the polymer does not prematurely react with the initiator. To form the membrane, the two components are mixed and allowed to react to form the polymer.

The polymer generally has a weight-average molecular weight from about  
25 20,000 to about 150,000. Preferably, the polymer has a weight average molecular weight from about 45,000 to about 65,000.

When applied to a surface, the membrane should be at least about 1.5mm thick. Preferably, the membrane is about 2mm to about 6mm thick.

One property of the membrane is elongation, or the ability to be extended without breaking. It is defined as the percent increase in length of a membrane before it breaks (ASTM D638). It is desired to achieve the desired degree of elongation in the shortest possible time. Preferably, the membrane has an elongation greater than  
5 about 25 % after 24 hours from being formed. More preferably, the membrane has an elongation greater than about 50 % after 8 hours. Most preferably, the membrane has an elongation greater than about 75 % after 2 hours.

Another property of the membrane is tensile strength. Tensile strength is the  
10 maximum force that a membrane can withstand before breaking (ASTM D638). It is desired to achieve a high tensile strength. Preferably, the membrane has a tensile strength greater than about 1 MPa after 24 hours. More preferably, the membrane has a tensile strength greater than about 1 MPa after 6 hours. Most preferably, the membrane has a tensile strength greater than about 1 MPa after 30 minutes or less.

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The membrane also has the property of adhesion, or, the ability to adhere to a substrate to which it is applied. Adhesion is measured as the force required to remove the membrane from a surface (ASTM D4142). It is desired to achieve the desired degree of adhesion in the shortest amount of time. Preferably, the membrane has an  
20 adhesion strength greater than about 0.5 MPa after 24 hours. More preferably, the membrane has an adhesion strength greater than about 1 MPa after 8 hours. Most preferably the membrane has an adhesion strength greater than about 0.5 MPa after 30 minutes or less.

The membrane is also capable of quick setting. By "quick setting", it is meant  
25 that the membrane achieves at least one of the tensile, elongation, and adhesive properties within the time referenced above.

It is also desired that the membrane have a useful service life greater than one year. Also, during this time, it is desired that the membrane not become brittle, not  
30 be affected by high and low humidity, and be able to be applied in dry to damp conditions.

Because the membrane may be applied underground in a mine, it is desired that membrane be non-toxic to human contact.

5 In another embodiment of the present invention there is provided a method of reinforcing exposed surfaces in an excavation with a polymeric structural support membrane. The method includes providing a mixture of a monomer, a self-extinguishing agent an initiator, and optionally a crosslinking agent, reacting the mixture, and then applying the reacted mixture to the exposed surface. This method provides for applying the above-described polymeric structural support membrane on  
10 an exposed surface.

The mixture can be applied by spraying, brushing, or rolling to provide the polymeric structural support membrane on an exposed surface.

## 15 SPECIFIC EMBODIMENTS OF THE INVENTION

The above described invention can be demonstrated by, but is not limited to, the following examples.

### 20 EXAMPLE 1

Several mixtures of membrane material were formulated. The formulations are listed below in Table 1A. The amounts are listed as percent by weight in the formulation. Additionally, the formulation contained about 3% by weight dibenzoyl peroxide as initiator and about 4 to about 5% by weight dimethyl aniline as a reaction  
25 rate modifier.

The materials in the Table 1A are as follows:

A - hydroxypropyl methacrylate (monomer)

B - ethoxylated nonyl phenol (emulsifier)

C - styrene n-butyl acrylate copolymer (crosslinking agent)

5 D - styrene n-butyl acrylate copolymer with higher styrene content  
(crosslinking agent)

E - triphenyl phosphate (self-extinguishing agent)

F - 1,6-hexanediol dimethacrylate (crosslinking agent)

G - ethoxylated bisphenol dimethacrylate (crosslinking agent)

10 H - lauryl methacrylate (plasticizer)

I - stearyl methacrylate (plasticizer)

J - polyethylene glycol dimethacrylate (crosslinking agent)

TABLE 1A

Mix	A	B	C	D	E	F	G	H	I	J
1	64.5	3.3	3.9	0	25	3.3	0	0	0	0
2	65	2.6	3.9	0	25.2	3.3	0	0	0	0
3	65.6	3.9	2	0	25.3	3.2	0	0	0	0
4	63.2	3.2	5.9	0	24.5	3.2	0	0	0	0
5	64.5	3.3	3.9	0	25	3.3	0	0	0	0
6	63.6	3.2	3.9	0	26.2	3.2	0	0	0	0
7	65.6	3.3	3.9	0	23.8	3.3	0	0	0	0
8	65.7	3.3	3.9	0	25.4	1.7	0	0	0	0
9	63.7	3.2	3.8	0	24.6	4.7	0	0	0	0
10	65.7	3.3	3.9	0	25.4	0	1.7	0	0	0
11	64.7	3.2	3.9	0	25	0	3.2	0	0	0
12	63.7	3.2	3.8	0	24.6	0	4.7	0	0	0
13	63.3	3.2	3.8	0	24.5	3.2	0	2.1	0	0
14	63.3	3.2	3.8	0	24.5	3.2	0	0	2.1	0
15	65.9	3.3	0	2	25.5	3.3	0	0	0	0
16	64.7	3.2	0	3.9	25	3.2	0	0	0	0
17	63.4	3.2	0	5.7	24.5	3.2	0	0	0	0
18	64.7	3.2	3.9	0	25	3.2	0	0	0	0
19	64.7	3.2	3.9	0	25	3.2	0	0	0	0
20	64.7	3.2	3.9	0	25	3.2	0	0	0	0
21	64.7	3.2	3.9	0	25	3.2	0	0	0	0
22	65.7	3.3	3.9	0	25.4	0	0	0	0	1.7
23	64.7	3.2	3.9	0	25	0	0	0	0	3.2
24	63.7	3.2	3.8	0	24.6	0	0	0	0	4.7
25	61.2	3.7	3.7	0	27.8	3.7	0	0	0	0

The above samples were prepared as films. The films were dumbbell-shaped, 16mm wide along the test section, had an effective test length of 53mm, and had a total length of 93mm. The films were from about 3 to 4 mm thick. The tests that were performed were tensile strength (ASTM D638) after 1 hour, percent elongation (ASTM D638) after 1 hour, and water absorption at 24 hours. The water absorption was measured by weighing a film, immersing the film in water for 24 hours, removing the film and blotting it dry with a towel, and then reweighing the film. The percent increase in weight was recorded. The temperature in the laboratory during the testing varied. Five samples films were prepared and the test results of the five films were averaged. The results of the testing are listed below in Table 1B.

TABLE 1B

Mix	Temperature during the test (°C)	Average Tensile Strength after 1 hour (Mpa)	Average Elongation after 1 hour (%)	Water absorption at 24 hr (%)
1	20	6.3	58	1.6
2	21	6.4	62	13.6
3	21	6.2	72	3.9
4	22	6.8	61	3.1
5	22	4.4	74	5.0
6	23	4.6	83	5.5
7	24	5.3	67	3.1
8	24	3.9	127	3.7
9	23	5.1	55	3.2
10	24	3.9	219	7.1
11	24	3.4	178	4.4
12	24	3.9	157	3.2
13	24	3.7	84	1.6
14	24	3.8	74	3.6
15	24	4.2	90	3.4
16	24	2.6	100	2.6
17	19	6.2	85	4.0
18	23	3.4	76	3.2
19	23	3.9	68	4.7
20	22	5.5	64	3.2
21	21	6.7	46	6.6
22	21	5.2	117	5.6
23	21	5.6	111	6.0
24	20	6.1	110	5.3
25	24	3.5	99	3.2

The results in Table 1B show that the amount of each material in the membrane has an effect on tensile strength, elongation, and water absorption. By varying the amounts of the materials in the membrane, the properties of the membrane can be adjusted to provide for particular properties for a desired application.

The adhesion was tested using mix numbers 10, 17, and 23 (ASTM4142). The substrate used for the adhesion tests was dolorite. Adhesion results were 2.0 MPa, 1.2 MPa, and 0.8 MPa, respectively.

## EXAMPLE 2

Several two-component membranes were formulated. The formulations are listed below in Table 2A. The amounts are listed as percent by weight in the combined formulation. The materials listed below are formulated in the component indicated.

Materials in table are as follows:		<u>Component</u>
	A - hydroxypropyl methacrylate (monomer)	1
	B - triphenyl phosphate (self-extinguishing agent)	1 and 2
10	C - ethoxylated nonyl phenol (emulsifier)	1
	D - acrylic-styrene emulsion (crosslinking agent)	1
	E - hydroxypropyl cellulose	1
	F - exfoliated graphite (self-extinguishing agent)	1
	G - tetra alkyl ammonium hectorite clay (rheology modifier)	1 and 2
15	H - titanium dioxide (colouring agent)	1
	I - fumed silica (rheology modifier)	1 and 2
	J - benzoyl peroxide (initiator)	2
	K - N,N-dimethyl-p-toluidine (reaction rate modifier)	1
	L - ethoxylated(4) bisphenol A dimethacrylate (crosslinking agent)	1
20	M - (10)ethoxylated(10) bisphenol A dimethacrylate (crosslinking agent)	1



TABLE 2A

Material	Mix 2-1	Mix 2-2	Mix 2-3	Mix 2-4	Mix 2-5	Mix 2-6
A	59.6%	58.7%	59.6%	58.7%	39.5%	39.5%
B	26.8%	26.4%	26.8%	26.4%	31.7%	31.7%
C	2.7%	2.6%	2.7%	2.6%	0.0%	0.0%
D	3.0%	2.9%	3.0%	2.9%	0.0%	0.0%
E	0.5%	0.5%	0.5%	0.5%	0.0%	0.0%
F	0.0%	0.0%	0.0%	0.0%	5.1%	5.1%
G	0.0%	0.0%	0.0%	0.0%	9.3%	9.3%
H	0.0%	0.0%	0.0%	0.0%	0.7%	0.7%
I	0.0%	0.0%	0.0%	0.0%	2.6%	2.6%
J	6.0%	5.9%	6.0%	5.9%	1.6%	1.6%
K	0.0%	0.0%	0.0%	0.0%	0.3%	0.3%
L	1.5%	2.9%	0.0%	0.0%	0.0%	0.0%
M	0.0%	0.0%	1.5%	2.9%	9.2%	9.2%

The above samples were prepared as films and tested as in Example 1 for tensile strength and elongation. The results are listed below in Table 2B.

5

TABLE 2B

Mix No.	Average Tensile Strength after 1 hour (MPa)	Average Elongation after 1 hour (%)
2-1	5.3	49
2-2	5.7	57
2-3	4.5	101
2-4	4.8	132
2-5	4.2	142
2-6	3.5	153

The results in Table 2B show the effect on tensile strength, elongation, and water absorption by varying the amounts of each material in the membrane. By varying the amounts of the materials in the membrane, the properties of the membrane can be adjusted to provide for particular properties for a desired application.

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Additionally, the ratio of the first component to the second component was varied to determine the effect on tensile strength and elongation. The formulation for Mix 2-5 was selected. The comparison of ratio was based on 2.8 to 1 parts component 1 to component 2 by weight. The samples were prepared as films and tensile strength and elongation were tested as in Example 1. The results are listed below in Table 2C.

TABLE 2C

Mix Ratio	Average Tensile Strength after 1 hour (MPa)	Average Elongation after 1 hour (%)
50% more Component 2	1.4	72
25% more Component 2	1.8	98
10% more Component 2	2.5	114
2.8 to 1 parts Component 1 to Component 2 by weight	3.1	126
10% less Component 2	3.6	115
25% less Component 2	5.3	105
50% less Component 2	8	10

The results show that the elongation reaches a maximum at a ratio of about 2.8 to 1 parts component 1 to component 2, while tensile strength increases with decreasing amount of component 2.

### EXAMPLE 3

Additional two component membranes were formulated. The formulations are listed below in Table 3A. The amounts are listed as percent by weight in the combined formulation. The materials listed below are formulated in the component indicated.

Materials in table are as follows:

Component

A - hydroxypropyl methacrylate (monomer)	1
B - triphenyl phosphate (self-extinguishing agent)	1 and 2
C - (10)ethoxylated(10) bisphenol A dimethacrylate (crosslinking agent)	1
D - tetraalkyl ammonium hectorite clay (rheology modifier)	1 and 2
E - exfoliated graphite (self-extinguishing agent)	1
F - fumed silica (rheology modifier)	1 and 2
G - titanium dioxide (coloring agent)	1
H - N,N-dimethyl-p-toluidine (reaction rate modifier)	1
I - benzoyl peroxide (initiator)	2

TABLE 3A

Material	Mix 3-1	Mix 3-2	Mix 3-3	Mix 3-4
A	47.4%	48.3%	46.4%	44.2%
B	23.7%	24.1%	26.5%	29.3%
C	11.9%	12.1%	11.6%	11.1%
D	13.5%	13.7%	13.5%	13.2%
E	0.0%	0.0%	0.0%	0.0%
F	1.9%	0.0%	0.0%	0.0%
G	0.3%	0.5%	0.5%	0.5%
H	0.1%	0.2%	0.2%	0.1%
I	1.2%	1.2%	1.3%	1.6%

The above samples were prepared as films and tested as in Example 1 for  
 5 tensile strength and elongation. The results are listed below in Table 3B.

TABLE 3B

Mix No.	Average Tensile Strength after 1 hour (MPa)	Average Elongation after 1 hour (%)
Mix 3-1	5	45
Mix 3-2	9.5	59
Mix 3-3	7	76
Mix 3-4	4.5	82

The results in Table 3B show the effect on tensile strength, elongation, and water absorption by varying the amounts of each material in the membrane. By  
5 varying the amounts of the materials in the membrane, the properties of the membrane can be adjusted to provide for particular properties for a desired application.

The present invention therefore is demonstrated to be capable of providing an excavation polymeric structural support membrane.

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It should be appreciated that the present invention is not limited to the specific embodiments described above, but includes variations, modifications and equivalent embodiments defined by the following claims.

## CLAIMS

1. A polymeric excavation structural support membrane comprising a polymer that is a initiator-induced reaction product of monomer; a self-extinguishing agent; and optionally at least one of a cross-linking agent, a rheology modifier,  
5 reaction rate modifier, plasticizer, emulsifier, defoamer, filler, wet surface adhesion modifier, and coloring agent; wherein the monomer is selected from the group consisting of alkyl ester acrylates, alkyl ester methacrylates, and mixtures thereof; wherein the membrane has a tensile strength, a thickness, and a molecular weight sufficient to provide support to exposed surfaces in an  
10 excavation.
2. The polymeric structural support membrane of claim 1, wherein the membrane comprises a polymer that is a reaction product of a monomer, an initiator and a crosslinking agent; a self-extinguishing agent; and optionally at least one of a  
15 rheology modifier, reaction rate modifier, plasticizer, emulsifier, defoamer, filler, wet surface adhesion modifier, and coloring agent; wherein the monomer is selected from the group consisting of monofunctional alkyl ester acrylates, monofunctional alkyl ester methacrylates, and mixtures thereof.
3. The polymeric structural support membrane of claim 1 or 2, wherein the  
20 polymer is present in an amount from about 30% to about 70% by weight of the membrane, the self-extinguishing agent is present from about 5% to about 40% by weight of the membrane, the initiator is present from about 1 to about 10% by weight of the monomer.
4. The polymeric structural support membrane of claim 1 or 2, wherein, if  
25 present,
  - a. the crosslinking agent is present up to about 30% by weight of the monomer;
  - b. the rheology modifier is present up to about 10% by weight of the monomer;
  - c. the emulsifier is present up to about 5% by weight of the monomer;

- d. the plasticizer is present up to about 40% by weight of the monomer;
  - e. the filler is present up to about 40% by weight of the monomer;
  - f. the wet surface adhesion modifier is present up to about 3% by weight of the monomer;
  - 5 g. the coloring agent is present up to about 3% by weight of the monomer;
  - h. the defoamer is present up to about 3% by weight of the monomer; and
  - i. the reaction rate modifier is present up to about 10% by weight of the monomer.
5. The polymeric structural support membrane of claim 1 or 2, wherein the  
10 polymer has a weight-average molecular weight from about 20,000 to about 150,000.
6. The polymeric structural support membrane of claim 1 or 2, wherein the membrane is characterized by at least one of:
- 15 j. an elongation greater than about 25% after 24 hours from being formed;
  - k. an elongation greater than about 50% after 8 hours from being formed;
  - l. an elongation greater than about 75% after 2 hours from being formed;
  - m. a tensile strength greater than about 1 MPa after 24 hours from being formed;
  - 20 n. a tensile strength greater than about 1 MPa after 6 hours from being formed;
  - o. a tensile strength greater than about 1 MPa no longer than 30 minutes from being formed;
  - p. an adhesion strength greater than about 0.5MPa after 24 hours from  
25 being formed;
  - q. an adhesion strength greater than about 1 MPa after 8 hours from being formed; and
  - r. an adhesion strength greater than about 0.5 MPa no longer than 30 minutes from being formed.

7. The polymeric structural support membrane of claim 1 or 2, wherein the membrane is a reaction product of a first component and a second component; wherein the first component comprises monomer, and optionally a crosslinking agent, a reaction rate modifier, a self-extinguishing agent, a rheology modifier, filler, and a defoamer; and the second component comprises an initiator, and optionally a self-extinguishing agent, a rheology modifier, and a defoamer.
8. A method of reinforcing exposed surfaces in an excavation with a polymeric structural support membrane comprising providing a polymeric structural support membrane mixture as in any of claims 1-7, and applying said mixture to an exposed surface in an excavation.
9. A polymeric structural support membrane formed from the process comprising:
- s. reacting a monomer, an initiator and a self-extinguishing agent; and optionally at least one of a crosslinking agent, a rheology modifier, reaction rate modifier, plasticizer, emulsifier, defoamer, filler, wet surface adhesion modifier, and coloring agent to form a mixture; wherein the monomer is selected from the group consisting of alkyl ester acrylates, alkyl ester methacrylates, and mixtures thereof;
  - t. applying the mixture to an exposed surface in an excavation; wherein the membrane has a tensile strength, a thickness, and a molecular weight sufficient to provide support to the exposed surfaces in the excavation.
10. The polymeric structural support membrane of claim 9, wherein the tensile strength is at least 1 MPa, the thickness is about 1.5mm to about 6mm, and the weight average molecular weight is about 20,000 to about 150,000.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU00/00460

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int. Cl. <sup>7</sup> : C08L 33/08, 33/10; C08F 2/44; E21D 19/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC: C08L 33/08, 33/10; C08F 2/44; E21D 19/00.		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU:IPC AS ABOVE		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT WPAT AND JPAT: ACRYLATE, METHACRYLATE, FIRE RETARDANT, MEMBRANE, PHOSPHATE, GRAPHITE, EXCAVATION, MINING		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DERWENT WPAT ONLINE ABSTRACT NO. 1999-604985/52 CLASS A14, E11, G03 JP 11263894 A (ZEON KASEI KK) 28 SEPTEMBER 1999 ABSTRACT	1-7
P,X	DERWENT WPAT ONLINE ABSTRACT NO. 2000-021364/02 CLASS A87, E37, F06 NL 1010837 A (KYOWA KK) 13 JULY 1999 ABSTRACT	1-7
X	DERWENT WPAT ONLINE ABSTRACT NO. 90-023015/04 CLASS A93, L02 DE 3822088 A (BAYER AG) 11 JANUARY 1990 ABSTRACT	1-7
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 8 June 2000		Date of mailing of the international search report 26 JUN 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer B Crouch Telephone No : (02) 6283 2060



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00460

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DERWENT WPAT ONLINE ABSTRACT NO. 89-348262/47 CLASS A93, E19, G02 ZA 8809444 A (CERTIFIED TECHN COR) 30 AUGUST 1989 ABSTRACT	1-10

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU00/00460**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member	
NL	1010837	CN	1236840	JP	11236570
					END OF ANNEX